Multiplet Structures of Charged Fullerenes

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Abstract. We calculated multiplet splittings for positively and negatively charged fullerene ions within the CAS SCF method, and extracted model parameters for the intramolecular Hamiltonian. The method treats correctly the symmetry of ground and excited states for partially occupied degenerate molecular orbitals. We compare our results to previous calculations by the LDA, MNDO and model SCF methods. The multiplet averaged Coulomb parameter U is about 3.1 eV for electrons and 3.2 eV for holes. The Hund's rule exchange parameter J is found to be 113 meV for electrons and 192 meV for holes.

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1. Introduction

Despite the fact that only very few successful attempts to produce hole-doped crystalline fullerene have been reported (see Panich *et al.* [1, 2, 3]), it is interesting to investigate the properties of such compounds. Their physical behavior will to large parts be determined by the ground state properties and the low energy excitations of positively charged molecular ions. Besides that, fullerene molecular ions can be realized in solution, and to some extent also in vacuum.

The physics of charged fullerenes is determined by their high orbital degeneracy (3 in case of electron doping and 5 in case of hole doping for C_{60}), and the resulting interplay between the Jahn-Teller (JT) effect and Hund's rule. The latter favors high-spin ground states while the former splits the orbital degeneracy by a JT distortion of the molecule, leading to a low-spin ground state. This in turn will influence the tendency of hole-doped systems to become e.g. insulating or magnetic or superconducting.

This interplay can be observed in the electron-doped compounds, some of which show metallic behavior and can become superconducting, such as A_3C_{60}, (A=K, Rb, Cs) [4, 5], others are insulating like, e.g. Na_2C_{60} [6] or A_4C_{60} [7]. Recent data on the charge transfer compounds $(AsF_6)_2C_{60}$ and $(SbF_6)C_{60}$, which contain nominal $C_{60}{}^{2+}$ seem insulating and compatible with a magnetic ground state of the $C_{60}{}^{2+}$ ions [3].

In this paper we report a theoretical study of the multiplet structures of isolated $C_{60}^{\pm n}$ ions. Due to the open shell nature of the charged molecules, the multiplet energies cannot be obtained reliably by more standard methods such as ROHF (*Restricted Open-Shell Hartree-Fock*) or LDA (*Local Density Approximation*) calculations. We apply *ab initio* CAS SCF (*Complete Active Space Self-Consistent Field*) calculations, which are the appropriate generalization of the Hartree-Fock (HF) method to orbitally degenerate systems [8].

We compare our results with previous studies, which were based on the semi-empirical calculations [9, 10], model-SCF calculations [11], limited CI (*Configuration Interaction*) calculations [12, 13] and on constrained LDA calculations [14].

2. Model Hamiltonian

As the starting point for describing the low energy physics of doped fullerenes one needs a model Hamiltonian which describes the interactions among the t_{1u} electrons in case of electron-doping and or the h_u holes in case of hole-doping, coupled to the vibrations of atoms in the molecule. Such a model was recently proposed in Ref. [14] and shall only be briefly introduced here.

The model Hamiltonian for a single molecule reads

$$\hat{H} = \hat{H}_0 + \hat{H}_{\text{vib}} + \hat{H}_{\text{e}-\text{vib}} + \hat{H}_{\text{e}-\text{e}}, \tag{1}$$

where

$$\hat{H}_0 \quad = \epsilon \sum_{\sigma m} \hat{c}_{\sigma m}^{\dagger} \hat{c}_{\sigma m}, \tag{2}$$

$$\hat{H}_{\text{vib}} = \sum_{i\Lambda\mu} \frac{\hbar\omega_{i\Lambda}}{2}(\hat{P}_{i\Lambda\mu}^2 + \hat{Q}_{i\Lambda\mu}^2), \tag{3}$$

$$\hat{H}_{\text{e-vib}} = \sum_{\sigma m m'} \sum_{r\,i\Lambda\mu} \frac{g_{i\Lambda}^r \hbar\omega_{i\Lambda}}{2} C_{mm'}^{r\Lambda\mu} \, \hat{Q}_{i\Lambda\mu} \, \hat{c}_{\sigma m}^\dagger \hat{c}_{\sigma m'}, \tag{4}$$

$$\hat{H}_{\text{e-e}} = \frac{1}{2} \sum_{\sigma,\sigma'} \sum_{\substack{mm' \\ nn'}} w_{\sigma,\sigma'}(m, m'; n, n') \, \hat{c}_{\sigma m}^\dagger \hat{c}_{\sigma' m'}^\dagger \, \hat{c}_{\sigma' n'} \hat{c}_{\sigma n}, \tag{5}$$

are respectively the single-particle Hamiltonian, the molecular vibration energy in the harmonic approximation, the electron-vibration coupling in the linear JT approximation [15, 16], and the mutual Coulomb repulsion between the electrons. The $\hat{c}_{\sigma,m}^\dagger$ denote the creation operators of either a hole in the h_u HOMO (*Highest Occupied Molecular Orbital*) or an electron in the t_{1u} LUMO (*Lowest Occupied Molecular Orbital*), described by the single-particle wave function $\varphi_{m\sigma}(\mathbf{r})$. The index σ is the spin projection, m and n label the component within the degenerate electronic HOMO/LUMO multiplet, and i counts the vibration modes of symmetry Λ (2 A_g, 6 G_g and 8 H_h modes). $C_{mn}^{r\Lambda\mu}$ are Clebsch-Gordan coefficients of the icosahedral group, for coupling h_u (holes) or t_{1u} (electrons) states to vibrations of symmetry Λ. The index $r =1,2$ is a multiplicity label, relevant for H_g modes only [15, 17]. $\hat{Q}_{i\Lambda\mu}$ and $\hat{P}_{i\Lambda\mu}$ are the molecular vibration coordinates and conjugate momenta.

The Coulomb matrix elements are defined by:

$$w_{\sigma,\sigma'}(m, m'; n, n') = \int \mathrm{d}^3r \int \mathrm{d}^3r' \, \varphi_{m\sigma}^*(\mathbf{r}) \, \varphi_{m'\sigma'}^*(\mathbf{r}') \, u_{\sigma,\sigma'}(\mathbf{r}, \mathbf{r}') \, \varphi_{n\sigma}(\mathbf{r}) \, \varphi_{n'\sigma'}(\mathbf{r}'), \tag{6}$$

where $u_{\sigma,\sigma'}(\mathbf{r}, \mathbf{r}')$ is a generally screened Coulomb interaction. In Ref. [14] it was demonstrated that this interaction can, without loss of generality in the given subspace, be expressed in terms of a minimal number of physical parameters as:

$$\hat{H}_{\text{e-e}} = \frac{1}{2} \sum_{rr'\Lambda} F^{rr'\Lambda} \left(\sum_{\mu} \hat{w}^{r\Lambda\mu} \, \hat{w}^{r'\Lambda\mu} \right) - A\hat{n}, \tag{7}$$

where we defined the operators:

$$\hat{w}^{r\Lambda\mu} = \sum_{\sigma} \sum_{mn} C_{mn}^{r\Lambda\mu} \, \hat{c}_{\sigma m}^\dagger \hat{c}_{\sigma n}. \tag{8}$$

The single-particle term A, which results from rearranging the field operators, is a function of the Coulomb parameters defined below.

For electrons, the allowed Coulomb parameters, which generalize Slater's Coulomb parameters for atoms [18], arise from the product $t_{1u} \otimes t_{1u} = A_g \oplus H_g$ and we define thus $F_1 = F^{A_g}$ and $F_2 = F^{H_g}$. For holes, the relevant product is $h_u \otimes h_u = A_g \oplus G_g \oplus 2H_g$, giving rise to five parameters $F_1 = F^{A_g}, F_2 = F^{G_g}, F_3 = F^{1,1,H_g}, F_4 = F^{2,2,H_g}$ and the cross-term $F_5 = F^{1,2,H_g}$.

Interaction parameters with a more transparent meaning can be further introduced by looking at the averaged energies of a multiplet of given charge n and spin S. We find that

$$E_{\text{ave}}(n) = E_0 + \epsilon n + U \frac{n(n-1)}{2} \tag{9}$$

Table 1. Multiplet energies of the N electron states $(t_{1u})^N$ relative to the average energy $\epsilon N + UN(N+1)/2$.

N	$^{S(S+1)}\Lambda$	E_{mult}	N	$^{S(S+1)}\Lambda$	E_{mult}
2,4	^1A_g	$4J$	3	$^2T_{1u}$	$2J$
	^1H_g	J		^2H_u	0
	$^3T_{1g}$	$-J$		^4A_u	$-3J$

and

$$E_{\text{ave}}(n, S) - E_{\text{ave}}(n, S - 1) = 2\tilde{J}S \tag{10}$$

for both electrons and holes. To make contact with standard notation established historically, we rescale the exchange parameter for electrons as $J = 4\tilde{J}/5$, but keep $J = \tilde{J}$ for holes. It should be noted that here the on-site Coulomb repulsion parameter U is defined with respect to the multiplet averaged energies, while traditionally the "Hubbard" U (we call it U_0 in this work) is defined with respect to the ground-state energies of each charged system, i.e.

$$U_0 = I(n) - A(n) = I(n) - I(n+1) = E_0(n+1) + E_0(n-1) - 2E_0(n), \tag{11}$$

where $I(n)$ and $A(n)$ are respectively the ionization potential and the electron affinity of the n-charge ion.

The parameters introduced above can be expressed in terms of the original Coulomb-parameters, as:

$$U_{t_{1u}} = \frac{1}{3}(F_1 - F_2) \tag{12}$$

$$J_{t_{1u}} = 2F_2 \tag{13}$$

$$A_{t_{1u}} = \frac{1}{2}U + 2J \tag{14}$$

for electrons, and

$$U_{h_u} = \frac{F_1}{5} - \frac{4\,F_2}{45} - \frac{F_3}{9} - \frac{F_4}{9} \tag{15}$$

$$J_{h_u} = \frac{1}{6}F_2 + \frac{5}{24}(F_3 + F_4) \tag{16}$$

$$A_{h_u} = \frac{1}{2}U + \frac{8}{3}J \tag{17}$$

for holes. Analytic expressions for the eigenenergies of Hamiltonian 1 for holes were partly already reported in Ref. [14]. For completeness, we provide the eigenenergies for the N electron states in Table 1. Our scope in the rest of this paper will be the calculation of all these Coulomb parameters.

3. Computational details

In order to find the multiplet splittings we performed CAS SCF [8] calculations using the quantum chemistry package GAMESS [19]. If not stated otherwise, all calculations

Figure 1. The orbital degeneracies and splittings close to the HOMO-LUMO gap.
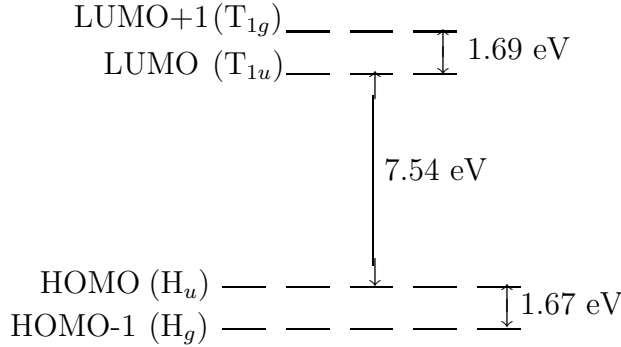
presented here have been performed using the 6-31 Gaussian basis set [6s3sp1sp]/[1s2sp] [20].

The energetic picture of the canonical orbitals, shown in Figure 1, motivates the choice of the active space. For the positive ions, we consider only states with holes delocalized in the 5-fold degenerate HOMO shell, and for the negative ions, the states with electrons in the 3-fold degenerate LUMO shell. This is justified by the large HOMO-LUMO gap of the isolated C_{60} molecule 7.54 eV. The separation between the HOMO shell and the HOMO-1 shell is 1.67 eV. A similar gap of 1.69 eV is found between the LUMO and LUMO-1 shells. We checked moreover that including the HOMO-1 and LUMO+1 shells respectively did not change the results for one and two holes in the HOMO and one and two electrons in the LUMO. Thus, all results are obtained with only one degenerate shell in the active space. The natural orbitals were optimized with respect to the averaged energy of all possible multiplet states regardless of the spin multiplicity. The geometry for the neutral C_{60} was optimized with the RHF (*Restricted Hartree-Fock*) method with perfect icosahedral symmetry. The hexagon and pentagon bond lengths obtained are 1.474 Å and 1.391 Å respectively. These are not far from the experimental crystalline values obtained from the neutron powder diffraction study (1.455 Å and 1.391 Å [21]), and ^{13}C NMR measurement of C-C bonds (1.450 Å and 1.40 Å [22]). ‖

‖ In order to further improve these results, one would need a bigger basis-set and inclusion of dynamical correlations in the calculations. The importance of these effects on the geometry and vibrational modes of C_{60} is discussed in Ref. [23]. Performing dynamically correlated calculations within the perturbation theory, for instance on the MP2 level (*second order Möller-Plesset*) [24, 25], would be computationally very expensive for the systems studied here. MP2 is a Rayleigh-Schrödinger perturbative method which uses the Hartree-Fock nonperturbed wave function and Hamiltonian as a zeroth order approximation. The perturbed functions depend on single-particle energies therefore it is a so-called "method with dynamical correlations". The semiempirical-approaches by the use of spectroscopic data for the estimation of two-electron integrals and the LDA method by the parametrization on the QMC data (*Quantum Monte Carlo*) also partially include the dynamical correlations. To estimate the effect of dynamical correlations, we report some results where we include them partially for the C_{60}^{1-} ion.

Although the JT effect is crucial for the physics of C_{60} ions [15], these changes of the geometry are relatively small and their influence on the Coulomb integrals (see Eq. (6)) should be fairly small. In the present calculations we ignore therefore those distortions and fix the geometry as frozen to that of neutral C_{60}.

4. Results

First we report the ground state energies for the C_{60} ions relative to the ground state of the neutral system. They are shown in Table 2, together with the ionization potentials and, if known, the corresponding experimental values. We report also the Hubbard U's, calculated from the ground state energies.

The calculated ionization potential (IP) in the $+1$ charged case 10.93 eV is in a good agreement with the experimental value 11.46$\pm$0.05 eV [26]. Also for the neutral molecule the calculated IP at 7.88 eV is close to the measured 7.6$\pm$0.2 eV [27]. Not surprisingly, the IP for the negative ion at 0.63 eV differs much from the experimental 2.65$\pm$0.05 eV [28]. The negatively charged ion is theoretically much more demanding since the additional electron moves in a less binding potential, is very delocalized and very sensitive to correlations with the other electrons. Therefore the basis set and the relaxation effects are more important in negative ions. To check the effects of the basis set and of additional correlations, we also performed calculations with the minimal basis set of order 3-21 ([6s3p]/[2s1p]) [29], which also allowed for a ROMP2 (*Restricted Open Shell MP2*) calculation, with frozen 175 occupied orbitals and 10+1 correlated electrons.

Table 2. Ground state energies (in eV), ionization potentials and Hubbard U's (U_0, obtained from the ground state total energies according to eq. (11)) for the charged fullerene.

Charge	E_{GS}	I	I_{exp}	U_0
-6	43.157	-14.974		
-5	28.183	-12.009		2.97
-4	16.174	-8.999		3.01
-3	7.175	-5.415		3.58
-2	1.760	-2.393		3.02
-1	-0.633	0.633	2.65 ± 0.05	3.03
0	0.000	7.883	7.6 ± 0.2	
1	7.883	10.925	11.46 ± 0.05	3.04
2	18.808	13.989		3.06
3	32.797	17.052		3.06
4	49.849	20.110		3.06
5	69.959	24.336		4.26
6	94.295	27.403		3.07
7	121.698	30.492		3.09
8	152.190	33.591		3.10
9	185.781	36.6728		3.08
10	222.453			

The restricted basis set reduced the IP of C_{60}^-, as expected, to -0.03 eV. Inclusion of the dynamical correlation increased the value from -0.03 eV to +0.43 eV. We checked that inclusion of 5-fold degenerate orbitals on HOMO-1 level in the active space does not change the IP for the C_{60}^- ion by more than 0.06 eV. Also the inclusion of higher 3-fold degenerate orbitals gives minor changes. The excitations from these orbitals contribute to the multiplets of negative ion with total weight smaller than 2% and do not change any of the splittings. The better agreement with experiment obtained by other authors by means of semiempirical approaches [9, 30, 31] for C_{60}^- could be partly due to the fact that the parameters used there are derived from spectroscopic data. C_{60}^{2-} ions were observed in gas phase measurements [32, 33] and found to be stable in semiempirical calculations [9, 30]. However the experimental results were questioned by other group [34]. In print of principle, our calculations are not ideally suited for negative ions. First of all, the weakly bound electron state is delicately sensitive to polarization and to correlations, not very accurate in DFT. Secondly, the basis set becomes critical unless it is extended very much, which is beyond our scopes. Earlier calculations by Razafinjanahary *et al.* [35] are probably of better quality in that respect. A comparison to the previous calculations by means of DFT (*Density Functional Theory*) given in Table 4 of Ref. [35] supports the importance of electronic correlations. The IPs collected in that paper strongly depend on the exchange-correlation functional as one can see from values: 2.0 eV [36], 1.9 eV [35], 2.7 eV [36] and 2.8 eV [37] for C_{60}^- and values: -1.3 eV [36], -1.2 eV [35], -0.4 eV [36] and -0.3 eV [37] for C_{60}^{2-} obtained respectively with functionals: $X\alpha$, VWN (Vosko-Wilk-Nusair), BH (Barth-Hedin) and PZ (Perdew-Zunger). Our IP of C_{60}^{3-} found to be -5.42 eV should be compared with value -4.4 eV obtained with the VWN functional from the modified MT (*Muffin-Tin Approximation*) calculations by Razafinjanahary *et al.* [35]. ¶

The bare molecular Hubbard U's (U_0) are all of the order of 3.01-3.10 eV for both electrons and holes (see Table 2). Exceptions are the 3-fold negative and the 5-fold positive systems. Here the U's are considerably larger. The parameters U_0 obtained for the charge n were derived from the ground state energies of molecules with charge $n-1$ and $n+1$. Due to the particle-hole symmetry, the multiplet splittings of ions with charge one more and one less than the charge at half-filling are identical (the energy gaps on right and left from half-filling are equal). This is not the case of any other charge, where the "neighboring" multiplet splittings are different and the ground energies of the charge multiplets which are more rich in the number of states, are lowered in comparison to the ground energies of multiplets with smaller number of states. The aforementioned asymmetry leads to smaller values of U_0 away from exact half filling.

¶ The question was raised in Ref. [35] about possible electron states trapped inside the C_{60} molecule. If such states existed, a calculation like the present where all basis functions are carbon-centered, and none is molecule-centered, could very well miss such a trapped state. However, the trapped state would not be missed in a plane-wave (PW) calculation. Direct comparison of our t_{1u} LUMO and t_{2g} LUMO+1 derived states with those of the PW calculations of C_{60} in Ref. [38, 39] shows perfect agreement, with no additional low laying states in the PW case that could be taken as trapped states (states with the spherical symmetry).

Table 3. Multiplet energies (in Merv) for 2,3 and 4 electrons in the (t_{1u}) LUMPY, and energies reconstructed from the model (eq. (11)-(13)) using the charge-averaged parameters eq. (9,10).

λ	N=2	N=4	Model	λ	N=3	Model
$^3T_{1g}$	-114.1	-112.7	-113.5	^4A_u	-340.7	-340.4
^1H_g	114.1	112.7	113.5	^2H_u	0.0	0.0
^1A_g	456.6	450.9	453.9	$^2T_{1u}$	227.1	226.9

Table 4. Multiplet energies (in meV) for 2,3,7 and 8 holes in the (h_u) HOMO, and energies reconstructed from the model (eq. (14)-(16)) using the charge-averaged parameters eq. (9,10).

λ	N=2	N=8	Model	λ	N=3	N=7	Model
$^3T_{bg}$	-134.8	-125.2	-133.8	$^4T_{bu}$	-388.9	-382.3	-390.3
$^3T_{ag}$	-127.9	-139.7	-128.7	$^4T_{au}$	-385.8	-394.8	-385.2
^3G_g	-122.4	-122.5	-123.8	^4G_u	-378.8	-382.0	-380.2
^1G_g	52.0	63.6	57.7	$^2T_{au}$	-113.6	-99.2	-109.1
^1H_g	57.4	67.1	62.2	$^2T_{bu}$	-110.5	-107.8	-104.0
^1H_g	463.3	448.4	455.9	^2H_u	-105.6	-95.3	-101.3
^1A_g	1022.3	1029.7	1026.0	^2H_u	-102.2	-91.3	-97.4
				^2G_u	191.2	189.1	190.1
				$^2T_{1u}, ^2T_{2u}$	199.7	196.0	197.7
				^2H_u	398.1	386.9	392.1
				^2G_u	399.1	388.1	393.1
				^2H_u	767.9	772.1	768.6

The key results of the above described CAS SCF calculations are the multiplet energies of the fullerene ions. They are reported in Table 3 for electrons and Tables 4 and 5 for holes. Since GAMESS does not support symmetries as high as icosahedral, the assignment of the symmetry labels to the states in CAS SCF calculations was done indirectly, using the degeneracies of the states. In this way, the three-fold degenerate T_1 and T_2 representations cannot be distinguished. However, due to the analytical results of the model Hamiltonian, reported in Ref. [14], they can be assigned once a certain sign of the parameter F_5 is chosen. Hence, in these cases we label the states by $T_{a/b}$ where a/b represents 1 or 2 respectively. In the negative ions, no such ambiguity arises.

We find that the spread of the multiplets is about 0.6 eV for all negatively charged states, 1.2 eV for 2, 3, 7 and 8 holes, and 2.3 eV for 4-6 holes. Comparing the spectra for N and 6-N electrons, or N and 10-N holes respectively, one finds that the particle-hole symmetry in the occupation of the degenerate orbitals is approximately preserved in both cases. [+]

The semi-empirical calculations for multiplets of C_{60}^{n-} ions and for C_{60}^{+1} and C_{60}^{+2} ions

[+] Clearly however, this approximate symmetry is a result of out single-orbital approximation, and would disappear once all other levels would be included. In this sense, it is mostly of academic significance.

Table 5. Multiplet energies (in meV) for 2,3,7 and 8 holes in the (h_u) HOMO, and energies reconstructed from the model (eq. (14)-(16)) using the charge-averaged parameters eq. (9,10).

λ	N=4	N=6	Model	λ	N=5	Model
^5H_g	-768.3	-770.1	-769.5	^6A_u	-1282.7	-1282.6
^3G_g	-395.7	-389.8	-393.1	^4H_u	-712.6	-712.4
^3H_g	-394.7	-388.9	-392.2	^2H_u	-331.3	-331.1
^1G_g	-209.5	-199.7	-204.9	^2G_u	-330.8	-330.6
^1A_g	-205.5	-196.2	-201.2	^4H_u	-318.7	-318.7
^3G_g	-197.0	-195.2	-196.2	^4G_u	-314.2	-314.2
$^3T_{bg}$	-194.9	-196.3	-195.6	^2A_u	-139.1	-139.0
$^3T_{ag}$	-193.9	-189.7	-192.1	^4G_u	-132.8	-132.8
^1H_g	86.2	88.9	87.7	^2G_u	-131.5	-131.4
$^1T_{ag}$	92.0	91.0	91.7	$^4T_{au}$	-127.7	-127.8
^1H_g	93.8	97.9	95.5	$^4T_{1u}$	-122.7	-122.7
$^1T_{bg}$	93.5	97.2	96.7	^2H_u	143.6	143.8
$^3T_{ag}$	103.5	100.6	100.6	^2H_u	156.1	156.1
^3H_g	103.3	98.3	101.9	$^2T_{bu}$	158.9	158.9
$^3T_{bg}$	104.0	100.6	102.4	^2H_u	159.0	159.0
^3H_g	105.9	100.6	103.4	$^2T_{au}$	162.9	162.8
^3G_g	382.6	382.0	383.4	$^2T_{au}$	164.3	164.4
^1A_g	384.3	383.8	383.4	^2H_u	166.9	166.9
$^3T_{ag}$	385.1	384.7	385.0	$^2T_{bu}$	167.9	167.9
$^3T_{bg}$	385.6	387.9	386.7	$^2T_{bu}$	443.9	443.7
^1G_g	392.3	388.8	390.9	$^2T_{au}$	453.4	453.4
^1H_g	564.3	569.9	567.2	^2G_u	455.7	455.6
^1G_g	578.4	581.1	580.2	^2G_u	460.1	459.9
^1H_g	590.4	583.1	587.2	^2A_u	463.9	463.6
^1G_g	591.3	585.2	588.3	^2G_u	646.8	646.7
^1H_g	970.3	966.9	969.0	^2H_u	651.3	651.1
^1A_g	1536.7	1540.7	1539.2	^2H_u	1026.3	1026.2

[9] give larger splittings than ours probably due to unequal occupation of degenerate orbitals. The limited CI calculations with HF reference orbitals do not take care of the right degeneracies due to the splitting of t_{1u} shell when it is partially occupied by the electrons. The discussion of this fact is given in Ref. [13]. The CAS SCF calculations are free of symmetry related problems. Also, excessively large splittings were obtained with the restricted configuration interaction constructed using the INDO (*Intermediate Neglect of the Diatomic Overlap*, for the method see [40]) orbitals [10].

Recently a complete analysis of the multiplets of all C_{60} ions was presented [11], where the multiplet energies were evaluated from a multipole expansion of the Coulomb interaction. The Coulomb integrals were calculated with respect to symmetry-adapted model wave functions. The obtained multiplet spectra are in good agreement with our results, apart from a larger T_1/T_2 splitting, and a change in the level ordering. We will comment on this point later, when discussing the Coulomb parameters extracted from

Figure 2. Average multiplet energies and the fitted parabola for the $(t_{1u})^N$ states for electrons and the $(h_u)^N$ states for holes.
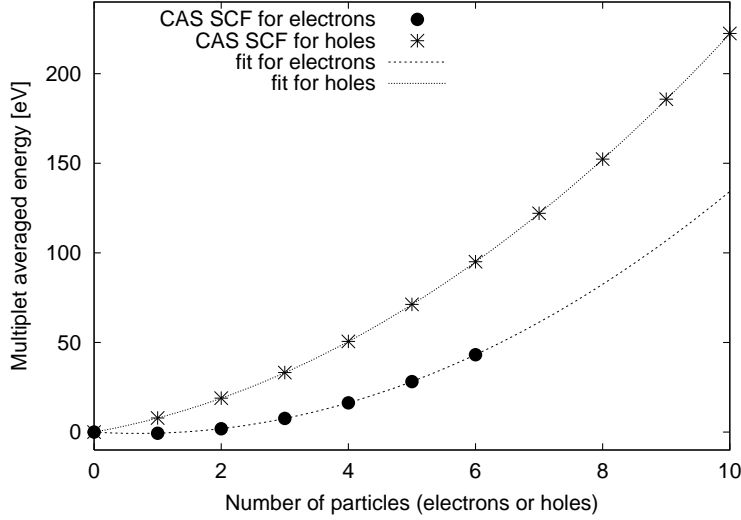
the present results.

We observe a degeneracy between the $^2T_{1u}$ and the $^2T_{2u}$ states of the three hole multiplets. This apparently accidental degeneracy is indeed well studied in the literature [41, 42, 43] and attributed to the permutational symmetry.

5. Determination of the model parameters

According to Eq. (9), the multiplet-averaged energies of the model are described by the parabola:

$$E_{\text{ave}}(n) = E_0 + (\epsilon - \frac{U}{2})n + U\frac{n^2}{2}, \tag{18}$$

where n denotes the number of electrons or holes respectively.

Figure 2 displays the calculated average energies, together with the fitted parabolas:

$$E_{\text{ave}}^{e^-}(n) = -61393.320 - 2.145n + 1.557n^2, \tag{19}$$
$$E_{\text{ave}}^{h^+}(n) = -61393.268 + 6.245n + 1.599n^2. \tag{20}$$

From these parabolas the average Coulomb repulsion U_{ave} and the single particle energies ϵ are obtained. These are displayed in Table 6.

This Coulomb repulsion U_{ave}, of about 3 eV for both electrons and holes, is in good agreement with previous calculations [44, 14]. The single-particle energies, extracted from the parabolas, are very close to the single-particle levels of the neutral system. It should be noted that this is not an obvious finding, since the single-particle energies, extracted from the fit, derive from a calculation of the charged molecules. In the model Hamiltonian, the first ionization potential is equal exactly to the single particle energy

Table 6. Coulomb parameters end Koopmans single particle energies for electrons and holes (in eV).

	U_{ave}	ϵ	ϵ_{RHF}
electrons	3.1141	-0.5881	-0.4898
holes	3.1928	-7.8477	-8.0270

Table 7. Exchange splitting J of the electron states $(t_{1u})^N$, for each charge N, as well as it's averaged value (ave). The values labeled by limited CI are extracted from [13], INDO+CI from [10], "direct" refers to Nikolaev *et.al.* [11], LDA to Lüders *et al.* [14], MNDO+CI to [30]. All parameters are given in meV.

Method	N=2	3	4	ave
CAS SCF	114.1	113.6	112.7	113.5
limited CI	29-146	8-388	8.5-380	15-305
INDO+CI	120	185	-	153
"direct"	-	-	-	99, 95
LDA	-	-	-	32
MNDO+CI	50	-	-	50

of the holes. In fact, Koopmans theorem states that the HOMO level gives a good approximation for the ionization potential. In general Koopmans theorem does not perform very well for the electron affinity, due to a bad description of the virtual states by means of the HF method (see [12] p. 127-128). Calculations involving charged states, in which the LUMO shell of the neutral molecule is actually occupied, should give much better values. Here we find, however, that the single particle energy of the electrons, determined from the fit, which represents the electron affinity of the model, is very close to the LUMO level obtained by means of the RHF method.

Next, for the N electron states $(t_{1u})^N$, only the exchange parameter J remains to be determined. Knowing the analytical eigenenergies (Table 1), it can be directly extracted from the calculated multiplets given in Table 3. The exchange constants Js, obtained in this way, are given in Table 7. We compare them to other results by means of the LDA method, and to model calculations ("direct" in Table 7) and to the limited CI method, and finally to the small configuration interaction performed on the INDO orbitals. Our results are close to those obtained by the model calculations [11], although slightly larger. By contrast the values of Hund's rule exchange J obtained by LDA is a factor of 3 smaller [14]. The reason for the large discrepancy with the LDA calculations is not clear. *

The J parameters shown in Table 7 for limited CI are extracted according to Table 1 from the multiplet splittings of either the lowest states or of the whole multiplet

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* This could be due to correlation effects included in the effective Kohn-Sham potential or due to the symmetry or self-interaction problems present in LDA calculations.

within the t_{1u} shell. These CI parameters depend strongly on the charge and the choice of states used for the derivation. This is due to the fact that the configuration interaction approach does not treat correctly the symmetry of t_{1u} shell, removing the 3-fold degeneracy when the shell is partially occupied by the electrons [13]. CAS SCF calculations give correct degeneracies and the obtained J parameters are independent on the charge and the choice of states (due to the multiplet structure showed in Table 1). The fact that limited CI calculations underestimate splittings of the lowest states and overestimate splitting of higher states is not only due to the broken symmetry, but also due to the use of HF single-particle orbitals optimized for the ground state. Contrary to that, in our CAS SCF calculations we optimized the molecular orbitals in such a way that the total energy averaged over all states within the multiplet was minimal.

Other authors, by means of the MNDO+CI method (*Modified Neglect of Diatomic Overlap*, for the method see [45]), derived $J = 30$ meV for the neutral C_{60} molecule and J=50 meV from the C_{60}^{-2} triplet-singlet splitting [30]. The *ab initio* SCF calculations point to a J value of order 100 meV [46]. The parameters obtained from the MNDO+CI method are smaller than the limited CI results probably due to the use of semi-empirical orbitals (direct fit on spectroscopic data) for the CI construction.

For the positively charged states, the situation is both more complicated, and less explored. Due to the uncertainty of the T_1, T_2 assignment and the multiple occurrence of states of the same symmetry but different energies, the parameters cannot be fitted directly to the multiplet energies. We therefore refer to the average energies for a given symmetry, shown in Table 8. As can be seen from this table, the averaging over the T_1 and the T_2 states depends only on F_2, F_3 and F_4, while F_5 determines T_1 - T_2 splitting only. The parameters F_2 - F_4 can be determined completely, while F_5 can only be found up to a sign. As it turns out, F_5 is however small enough to make this uncertainty irrelevant.

We fit the multiplet energies for each charge separately, allowing for charge-dependent model parameters, which are given in Table 9. The parameters F_2, F_3 and F_4 show a weak monotonic dependence on charge. This is in contrast to the result of Ref. [11] whose parameters are basically determined at $N=0$, and then used for all N. From this perspective it becomes clearer why the T_{1u}/T_{2u} splittings of Ref. [11] are much larger than ours.

The substantial difference of our CAS SCF results with the LDA parameters of Ref. [14] for hole-doped ions, also shown in Table 9, is similar to the discrepancy noted in the electron-doped case.

6. Summary

The central aim of this work is a calculation of all Coulomb parameters and multiplet energies for $C_{60}^{\pm n}$ ions including a proper treatment of the orbital degeneracies, within the icosahedral symmetry of C_{60}. This has been done within the CAS SCF framework.

The model parameters for positively charged C_{60} ions are substantially larger than

Table 8. The Coulomb multiplets for C_{60}^{N+}, averaged over states of the same representation, as a function of the e-e parameters. The model Hamiltonian (1) obeys particle-hole symmetry: therefore the multiplet energies for $N > 5$ holes equal those for $(10 - N)$ holes. The non particle-hole symmetric contribution $[\epsilon N + U N(N-1)/2]$ is left out in this table.

Ion	State symmetry	$E_{\mathrm{mult,ave}}(N, \Lambda, S)$
$N{=}2$	^1A_g	$\frac{8}{9}F_2 + \frac{10}{9}F_3 + \frac{10}{9}F_4$
	^1G_g	$\frac{1}{18}F_2 - \frac{5}{36}F_3 + \frac{25}{36}F_4$
	$^1H_g\ [\times 2]$	$\frac{2}{9}F_2 + \frac{13}{36}F_3 + \frac{1}{36}F_4$
	$^3T_{1g}$	$-\frac{4}{9}F_2 - \frac{5}{36}F_3 + \frac{7}{36}F_4 + \frac{\sqrt{5}}{2}F_5$
	$^3T_{2g}$	$-\frac{4}{9}F_2 - \frac{5}{36}F_3 + \frac{7}{36}F_4 - \frac{\sqrt{5}}{2}F_5$
	^3G_g	$\frac{7}{18}F_2 - \frac{5}{36}F_3 - \frac{23}{36}F_4$
$N{=}3$	$^2T_{1u}\ [\times 2]$	$-\frac{1}{12}F_2 - \frac{1}{24}F_3 + \frac{7}{24}F_4 - \frac{\sqrt{5}}{4}F_5$
	$^2T_{2u}\ [\times 2]$	$-\frac{1}{12}F_2 - \frac{1}{24}F_3 + \frac{7}{24}F_4 + \frac{\sqrt{5}}{4}F_5$
	$^2G_u\ [\times 2]$	$-\frac{1}{3}F_2 + \frac{7}{12}F_3 + \frac{1}{12}F_4$
	$^2H_u\ [\times 4]$	$\frac{5}{12}F_2 + \frac{5}{24}F_3 + \frac{5}{24}F_4$
	$^4T_{1u}$	$-\frac{2}{3}F_2 - \frac{5}{12}F_3 - \frac{1}{12}F_4 + \frac{\sqrt{5}}{2}F_5$
	$^4T_{2u}$	$-\frac{2}{3}F_2 - \frac{5}{12}F_3 - \frac{1}{12}F_4 - \frac{\sqrt{5}}{2}F_5$
	^4G_u	$\frac{1}{6}F_2 - \frac{5}{12}F_3 - \frac{11}{12}F_4$
$N{=}4$	$^1A_g\ [\times 3]$	$\frac{5}{9}F_2 + \frac{1}{2}F_3 + \frac{17}{18}F_4$
	$^1T_{1g}$	$\frac{1}{2}F_2 - \frac{1}{12}F_3 + \frac{1}{4}F_4 - \frac{\sqrt{5}}{2}F_5$
	$^1T_{2g}$	$\frac{1}{2}F_2 - \frac{1}{12}F_3 + \frac{1}{4}F_4 + \frac{\sqrt{5}}{2}F_5$
	$^1G_g\ [\times 4]$	$\frac{13}{24}F_2 + \frac{17}{48}F_3 + \frac{7}{48}F_4$
	$^1H_g\ [\times 5]$	$\frac{2}{15}F_2 + \frac{17}{30}F_3 + \frac{17}{30}F_4$
	$^3T_{1g}\ [\times 3]$	$\frac{1}{18}F_2 + \frac{1}{6}F_3 - \frac{1}{18}F_4$
	$^3T_{2g}\ [\times 3]$	$\frac{1}{18}F_2 + \frac{1}{6}F_3 - \frac{1}{18}F_4$
	$^3G_g\ [\times 3]$	$\frac{1}{18}F_2 - \frac{1}{4}F_3 + \frac{13}{36}F_4$
	$^3H_g\ [\times 3]$	$-\frac{1}{9}F_2 - \frac{2}{9}F_4$
	^5H_g	$-\frac{2}{3}F_2 - \frac{5}{6}F_3 - \frac{5}{6}F_4$
$N{=}5$	$^2A_u\ [\times 2]$	$-\frac{5}{18}F_2 + \frac{13}{36}F_3 + \frac{1}{36}F_4$
	$^2T_{1u}\ [\times 3]$	$\frac{4}{9}F_2 + \frac{5}{18}F_3 + \frac{1}{48}F_4 + \frac{\sqrt{5}}{3}F_5$
	$^2T_{2u}\ [\times 3]$	$\frac{4}{9}F_2 + \frac{5}{18}F_3 + \frac{1}{48}F_4 - \frac{\sqrt{5}}{3}F_5$
	$^2G_u\ [\times 5]$	$\frac{7}{45}F_2 + \frac{14}{45}F_3 + \frac{2}{45}F_4$
	$^2H_u\ [\times 7]$	$\frac{11}{63}F_2 + \frac{16}{63}F_3 + \frac{34}{63}F_4$
	$^4T_{1u}$	$\frac{2}{9}F_2 - \frac{5}{36}F_3 - \frac{17}{36}F_4 - \frac{\sqrt{5}}{2}F_5$
	$^4T_{2u}$	$\frac{2}{9}F_2 - \frac{5}{36}F_3 - \frac{17}{36}F_4 + \frac{\sqrt{5}}{2}F_5$
	$^4G_u\ [\times 2]$	$-\frac{4}{9}F_2 - \frac{5}{36}F_3 - \frac{11}{36}F_4$
	$^4H_u\ [\times 2]$	$-\frac{4}{9}F_2 - \frac{23}{36}F_3 - \frac{11}{36}F_4$
	^6A_u	$-\frac{10}{9}F_2 - \frac{25}{18}F_3 - \frac{25}{18}F_4$

Table 9. The model parameters for the positively charged states, determined from the multiplet spectra. We also give a comparison to the LDA calculations of Ref. [14] and the model (direct) calculations of Ref. [11]. All parameters are given in meV.

				CAS SCF						direct		LDA
	N=2	3	4	5	6	7	8	ave	II	III	
F_2	188.8	190.3	191.9	193.5	195.1	196.6	198.2	193.5	193	185	105
F_3	591.1	589.0	586.1	584.3	581.3	580.2	577.1	584.2	640	625	155
F_4	178.0	180.1	182.3	184.4	186.8	188.7	191.1	184.5	180	172	47
$|F_5|$	3.1	1.4	0.7	2.2	4.3	5.6	7.6	2.3*	13	13	0
J	191.7	191.9	192.1	192.4	192.5	193.0	193.1	192.4	203	197	60

the LDA results as in the negatively charged molecules. Our results on the other hand, are rather closer to model studies by Nikolaev [11]. A possible reason is that both approaches do not take into account the dynamical correlations, which are very important, as was shown in Ref. [23]. In the LDA and MNDO methods, where some dynamical correlations are included, the multiplet splittings are much reduced. The limited CI method led in previous calculations [13] to much smaller or much larger J values depending on the choice of states and on the charge case used for the derivation of parameters. This could be due to the artificially broken symmetries when the electrons occupy partially the molecular orbitals. The parameters obtained from the CAS SCF method, involving a correct treatment of symmetry, do not depend on the charge or choice of states within the multiplet used for the derivation.

The mean Coulomb parameters, U, obtained in this work from averaged multiplets, are for positively charged fullerenes about 3.2 eV. Similarly for the negative ions the obtained U parameters are about 3.1 eV. The charge specific Hubbard U_0 are generally close to the average, except at half filling where U_0 is not influenced by J. Here U_0=3.58 for C_{60}^{3-} and U_0=4.26 for C_{60}^{5+}.

The exchange parameters, J, for the negative ions are somewhat basis set dependent due to the localization effects discussed earlier, and their values are of about 114 meV for 6-31 basis set and 146 meV for the minimal basis set [29]. The more extended basis set contains more expanded Gaussians, while the smaller basis set constraining the electrons to a smaller volume, is likely to increase the exchange parameter J. The exchange parameters for hole-doped molecules are less basis set dependent: they are of order 192 meV for the 6-31 basis set and 208 meV for the minimal basis set. These values probably still represent an approximation in excess and it seems possible that a further slight decrease could be found with substantially larger basis sets. ♯

Experimentally, the multiplet structure of C_{60} ions in vacuum is still, as far as we know, inaccessible. In particular probing the magnetic state of ions in a beam

♯ The quality of Gaussian basis set type is more dependent on the well chosen exponents than on their number. There is no possibility for the saturation of a basis set similar to that can obtained with the plane-wave methods.

appears to be difficult. Probing charged fullerene ions embedded in a rare gas matrix would seem a better possibility, that could be explored with the purpose identifying the ground states properties for the various charged species, possibly with EPR ††. The Coulomb couplings of C_{60} ions play an important role in the solid state compounds. In particular in alkali fullerides the C_{60} molecule is negatively ionized while in Lewis acid fullerene salts [1, 2] it should be positively ionized. NMR longitudinal relaxation time data of basically all alkali fullerides indicate a "spin gap", separating the low spin C_{60} ion ground state from high spin excitations [47]. These spin gaps are typically 100-150 meV, compatible with a value of J of e.g. 50-70 meV. Comparison with our calculated value of 113 meV indicates an overestimate. While that may be due to a genuine solid state effect, we cannot rule out the possibility that the agreement could be improved by further extending the used basis set.

Finally, our predictions of a large J for positive fullerene ions, which also imply that they should be with great probability magnetic [14] should be directly accessible by further experiments on the acceptor salts [1, 2] as well as in the recently discovered C_{60}^{+2} and C_{60}^{+3} in solution [48].

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†† We owe this suggestion to G. Scoles.

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